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# Selectivity in analytical chemistry: two interpretations for univariate methods

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## Abstract

Selectivity is extremely important in analytical chemistry but its definition is elusive despite continued efforts by professional organizations and individual scientists. This paper shows that the existing selectivity concepts for univariate analytical methods broadly fall in two classes: selectivity concepts based on measurement error and concepts based on response surfaces (the response surface being the 3D plot of the univariate signal as a function of analyte and interferent concentration, respectively). The strengths and weaknesses of the different definitions are analyzed and contradictions between them unveiled. The error based selectivity is very general and very safe but its application to a range of samples (as opposed to a single sample) requires the knowledge of some constraint about the possible sample compositions. The selectivity concepts based on the response surface are easily applied to linear response surfaces but may lead to difficulties and counterintuitive results when applied to nonlinear response surfaces. A particular advantage of this class of selectivity is that with linear response surfaces it can provide a concentration independent measure of selectivity. In contrast, the error based selectivity concept allows only yes/no type decision about selectivity.

**Keywords:** analytical method, selectivity, error, interference

## 1. Introduction

Selectivity is one of the most important features of any analytical measurement. Without selectivity, i.e., if the measuring system responded to every substance in exactly the same way both qualitatively and quantitatively, it would not be possible to determine the concentration of any particular substance in a mixture. It is therefore logical to expect that analytical chemists have a widely accepted definition of selectivity of analytical methods. One would also expect that selectivity can be quantitated in a meaningful way, so that one could compare methods or method variants according to their selectivities.

### *1.1. Lack of a general definition and of a measure of selectivity*

Surprisingly, there is no generally accepted definition of selectivity in analytical chemistry, as shown by a recent review [1] and opinions diverge on its measurability. Some notable sources on the subject may be mentioned here. IUPAC has issued two recommendations and a technical report about the selectivity of general analytical methods [2-4]. It has also published selectivity definitions for particular methods, like potentiometry [5]. Guidelines for good laboratory practice require selectivity tests as part of method validation [6]. Metrological organizations define selectivity of measurements, including chemical ones [7, 8]. Clinical chemists appear to avoid the term selectivity and discuss interferences instead [9]. Textbooks of analytical chemistry usually devote very little space to selectivity and either redefine it in an approximate fashion or cite an IUPAC definition as it has been shown in a review [1]. No two of the mentioned sources define selectivity in exactly the same way, and none of them quantitates selectivity (except for some special techniques, like potentiometry).

The common denominator of some of the more recent recommendations by the mentioned professional organizations is that they consider an analytical method selective only if interferences do not influence the measurement result at all or at least not significantly [1]. This is a very strict and therefore quite safe definition but it has some disadvantages. Analytical chemists often develop methods which need to work reliably with a large variety of samples. The question is then how one can prove that a method will be selective (in the above very strict sense) in any future samples to be investigated. Thus the recommendations shift the burden to the analytical chemist who should define the range of future samples which can be selectively analyzed with a particular method. Recommendations for solving this task have been published in clinical chemistry [9], where the possible range of samples is more or less known, but similar recommendations are unlikely to be available or even possible for many other analytical problems.

The other disadvantage of the above mentioned definitions of selectivity is that while they may be satisfactory to characterize a fully developed method, they do not provide any quantitative measure of selectivity, not even an approximate one, which could guide the analytical chemist during method development in assessing and improving selectivity.

### *1.2. Narrowing of the problem*

Interferences to an analytical method can be of many different types. One may have sample matrix effects, analytical reagents may undergo side reactions with some sample components, etc. In a frequently encountered type of interference some components of the sample may influence the measured signal in the same way as the analyte. This is a typical problem with sensors, but spectral overlaps are of the same type, and in immunoassays we also have cross sensitivities. Even if we reduce the selectivity problem to such cases (as will be done in this paper), there is no general definition and measure of selectivity available. In individual analytical techniques, though, measures of selectivity have been defined for this type of interference. In absorption spectroscopy at a single wavelength, when the Lambert Beer law is valid for mixtures, the ratio of the respective molar absorbances of the analyte and the interferent, respectively, is an obvious measure of selectivity (see below). In ion selective electrode potentiometry selectivity coefficients have been widely used. Such selectivity concepts are typically based on the response characteristics of a technique or a device in mixed solutions of the analyte and the interferent(s).

This paper investigates if the common selectivity concepts used in analytical chemistry are meaningful, i.e. free of internal contradictions and mutually compatible. This work appears to be the first one to carry out such analysis. It is based among others on our experience with selectivity problems of ion selective electrodes [10-13], numerous method validations following guidelines for Good Laboratory Practice (GLP) [14, 15] and investigations about the selectivity of molecularly imprinted polymers [16, 17]. An impulse to this work has been given by important recent recognitions about the selectivity of ion selective electrodes [18-21] supported by a large body of experimental data. This study was also motivated by the work of M. Valcarcel and coworkers, who have also recognized the lack of general approaches to analytical selectivity and contributed to the clarification of the term selectivity [22].

## 2. Selectivity concepts and their properties in the univariate case

The problem discussed here is defined as follows. An analytical output quantity (a signal or an estimate of the analyte concentration, in either case a scalar quantity) is influenced by two components' concentration (Figure 1). One of these components is considered the analyte, the other the interferent. It is assumed that the response to the analyte alone is a strictly monotonous function of the analyte concentration. The interferent is supposed to affect the measurement in a similar manner to the analyte. This means here that the interferent alone would also give a monotonous calibration line with the same direction as the analyte. For simplicity we shall assume that the calibration lines are both monotonously increasing. It is also assumed that the addition of any of the two components to any mixture of them will increase the output value. All these assumptions are satisfied by many analytical methods.

The main ideas of the paper will be introduced by discussing first the simplest possible case, i.e., that of linear response in both concentration variables.

### 2.1. Linear response function

Let the measured signal,  $y$ , be a homogeneous linear function of the two concentrations, i.e.,

$$y = f(c_I, c_J) = k_I c_I + k_J c_J \quad (1)$$

Here I denotes the analyte, J the interferent,  $c$  with a subscript stands for the respective concentration. The  $k$ -s are constants. (The equation might also include an additive constant. This would, however, not influence the final result.) The analyst wants to estimate the concentration of the analyte from the measured signal,  $y$ . Without having any further information, this is not possible, because there are two unknown concentrations but only one equation. As additional information the analyst may know, for example, that the ratio of interferent to analyte concentration is less than a certain value in all future samples. In another scenario the analyst may ascertain by a quick test or by sample preparation that the interferent concentration is less than a certain value. In either case a rational approach is to consider at first the total signal to be due to the analyte alone. By this procedure one obtains the highest possible value of the analyte concentration (because of the monotonicity criteria made above) which is in accordance with the measured signal value and the additional condition at the same time. This estimate of the analyte concentration may be in error, but as will be shown immediately, the maximum of this error may be estimated and compared with the required tolerance level.

The biased estimate,  $\hat{c}_I$ , of the analyte concentration is calculated, as proposed above, by dividing the signal,  $y$ , by  $k_I$ , which is the slope of the calibration line in pure I solutions:

$$\hat{c}_I = \frac{y}{k_I} = \frac{k_I c_I + k_J c_J}{k_I} = c_I + \frac{k_J}{k_I} c_J \quad (2)$$

This equation shows that the estimate is biased, it is higher than the true  $c_I$ . The relative error of the estimate is:

$$\frac{\hat{c}_I - c_I}{c_I} = k_{IJ} \frac{c_J}{c_I} \quad (3)$$

where

$$k_{IJ} = \frac{k_J}{k_I} \quad (4)$$

The maximum committed relative error can be estimated now from the maximal ratio of the two concentrations if this was the additional information. If this error is higher than the maximum allowed error, the method needs improvement. For example the interferent concentration may be reduced by sample pretreatment. Alternatively, the analytical device may be improved. If in the end the error of the method is less than the predefined error limit, then one may say that the method is selective for I compared to J, at least as long as the additional information about the samples is valid.

Analytical chemists have, also other approaches to define selectivity. This is easily discussed for linear response functions [23]. One compares the values of  $k_I$  and  $k_J$  with each other. The method is considered selective for I if  $k_I > k_J$  (which is equivalent to  $k_{IJ} < 1$ ) and selective for J if  $k_I < k_J$ . If  $k_I = k_J$  the method is not selective. These criteria are very reasonable. The relationship between the two constants shows to which compound is the method more sensitive. This type of selectivity may be simply characterized by  $k_{IJ}$ , which may therefore be called a selectivity coefficient. One should note that this second type of selectivity depends only on the response surface (which in the linear case is a plane), and does not depend on additional information about the samples.

The two selectivity concepts discussed here, i.e. the one based on error considerations and the one based on sensitivities, are not very simply related to each other. This is immediately seen if one considers the following example. Let there be a linear response surface with  $k_{IJ} = 1$ . In a particular sample the ratio of the concentrations,  $c_J/c_I$ , should be 0.01. The relative error of the  $c_I$  measurement is then 1% as predicted by Equation 3. If this error level is tolerable, then the method will be considered selective (at least in the case of this sample and for any other samples where  $c_J/c_I < 0.01$ ), because the effect of the interferent on the measurement result is negligible. But according to the other, sensitivity based definition of selectivity, the method is not selective at all, since  $k_{IJ} = 1$ , i.e.,  $k_I = k_J$ .

The conclusion from these considerations is that two commonly used and apparently meaningful selectivity concepts are in conflict with each other even for the simplest possible response surface. This ambiguity may have contributed to the confusion about selectivity definitions.

Another conclusion is that the error based selectivity definition is only meaningful if we apply it either to a single sample instead of a method (which is not very practical in analytical chemistry), or if we make some tacit assumption about the composition of all future samples. Such assumptions may be difficult to check unless the composition of the samples is very restricted. In bioanalysis such restriction often exists for endogenous interferents which have a relatively narrow natural concentration range.

The selectivity concept based on the response surface parameter  $k_{IJ}$  has a great advantage: it provides a meaningful measure of selectivity for linear response surfaces in the form of  $k_{IJ}$ . It is also independent of assumptions about the sample composition. But it has also some disadvantages. Most importantly it cannot be transferred in a unique way to nonlinear response surfaces. This is so because  $k_{IJ}$  of a linear response surface can be interpreted in many different ways, which give the same result for a linear surface but usually different results for a nonlinear one. To give just two examples  $k_{IJ}$  can be interpreted as the ratio of the slopes of the separate calibration lines for I and J, respectively, or as the ratio of the two partial derivatives of  $y$  with respect to I and J, respectively.

A third approach to selectivity which is also intuitively appealing, consists of comparing the pure I and pure J concentrations, respectively, which belong to the same signal value. From Equation 1 these are easily obtained for linear response surfaces:

$$c_I = \frac{y}{k_I} \quad (5)$$

and

$$c_J = \frac{y}{k_J} \quad (6)$$

If  $c_I < c_J$  then the measurement may be regarded selective for I, since the same signal is caused by a smaller concentration of I than of J (and as assumed above the signal increases with concentration). From Equations 5 and 6 this type of selectivity for I occurs if  $k_{IJ} < 1$ , just like before. However, for nonlinear response surfaces this selectivity definition may have a complex relationship with the others.

## 2.2. General response function

In case of a more or less general response function (which still maintains monotonicity and smoothness as in Figure 1) the problems of defining selectivity and of estimating the measurement error become worse. Sensitivity, i.e., the partial derivative of the signal with respect to either concentration, is no more a constant as it was in the form of  $k_I$  and  $k_J$ , respectively, in the linear case. The ratio of sensitivities for I and J, respectively, is only a local quantity (changing with both  $c_I$  and  $c_J$ ) and not a universal constant.

Nonlinear response surfaces may complicate any statement about method selectivity. It is possible (as has been found, for example, in potentiometry [21]) that in certain ranges of  $c_I$  and  $c_J$  the method is selective for I and in other ranges for J. Thus one cannot always say that the method is selective for I or J, even if we consider only the response surface.

With some nonlinear surfaces a further type of selectivity has been defined, e.g., in potentiometry [18], which is conceptually different from those discussed so far. An interesting property of such surfaces is that given the parameters of the calibration line for the pure analyte I, the whole response surface (including the response to pure J) can be described by a single additional parameter. In potentiometry this parameter is the difference between the standard potentials measured in I and J solutions, respectively. This parameter (divided by a constant factor) has been called selectivity coefficient, although it does not describe selectivity in any of the above mentioned ways. However, it can be used to calculate any of those measures because it describes (together with the calibration parameters for I) the whole response surface.

### 2.3. Pseudo linear response functions

Since interpretation of selectivity becomes so difficult with nonlinear response surfaces, it is natural to ask if there are any practically existing nonlinear response surfaces which retain the simple properties of linear ones, with respect to selectivity. Interestingly, such surfaces exist. The Nicholsky equation in potentiometry (Equation 7) describes, for example, such a response surface if it is applied to two ions of identical charge.

$$E = E_I^0 + \frac{RT}{z_I F} \ln (a_I + k_{IJ} a_J^{z_I/z_J}) \quad (7)$$

(The notation is well known, only  $k$  is not in capital letter as in potentiometry.) It will be shown now that this equation is just one representative of a special class of functions well-behaved in matters of selectivity.

Let us recall that for linear response surfaces the relative error was expressed by Equation 3.

After simple rearrangement:

$$\hat{c}_I = c_I + k_{IJ} c_J \quad (8)$$

Similarly to the linear case, even if the response function is nonlinear, the biased estimate for the analyte concentration should be calculated from the measured signal by assuming that the concentration of the interferent is zero. Let us consider now only such response functions where for any  $(c_I, c_J)$  pair which gives the same signal  $y$  the relationship of Equation 8 is valid. Then:

$$y = f(c_I, c_J) = f(\hat{c}_I, 0) = f(c_I + k_{IJ} c_J, 0) \quad (9)$$

Here  $f$  means a general bivariate function. The right hand side of Equation 9 describes a bivariate response surface which need not be linear. It is special, however, because it is an apparently univariate function of the variable

$$c_I + k_{IJ} c_J \quad (10)$$

with  $k_{IJ}$  being a constant. Due to Equation 9 the error formula of Equation 3 will be valid for such functions. As a practical example the Nicholsky equation for two ions of equal valency  $z$  satisfies this criterion:

$$E = E_I^0 + \frac{RT}{zF} \ln (a_I + k_{IJ} a_J) \quad (11)$$

As immediately seen, for a constant value of  $E$  the value of  $a_I + k_{IJ} a_J$  is also constant. Note also that this equation is nonlinear.

One may call the response surfaces which satisfy Equation 9 pseudolinear surfaces. If a method has such a response surface then it can be characterized by a concentration independent selectivity coefficient. The measurement error is also easily calculated in this case, just like with linear response functions.

If the general condition of Equation 9 is not satisfied, one can in many practical applications limit the allowed range of the variables  $c_I$  and  $c_J$  so that in the limited range Equation 9 is valid, at least approximately. In certain analytical problems the analyte concentration can only move in a narrow range, so that the condition of Eq. 8

$$\hat{c}_I = c_I + k_{IJ}c_J$$

needs to be satisfied with a  $k_{IJ}$  that is not an overall constant but can be considered constant in a narrow range of the analyte concentration. In this range it must be then independent of the interferent concentration.

#### 2.4. The measure of selectivity

The previous discussion has shown that with certain response functions a constant and meaningful selectivity factor can be used. The constant  $k_{IJ}$  has been used here for easy comparison with the potentiometric selectivity coefficient. But  $k_{IJ}$  has a large value (i.e., much larger than 1) when the effect of the interferent on the signal is larger than that of the analyte. It would be therefore more appropriate to use the reciprocal of  $k_{IJ}$  to measure selectivity. In this paper we have used  $k_{IJ}$  for easy comparison with the Nicholsky equation (Equation 11).

### 3. Conclusion

Selectivity is an extremely important property of any analytical method but its definition and quantitation have still remained open questions. Many definitions of selectivity are possible and have indeed been used. They have been divided in this paper into two classes: definitions based on measurement error and definitions based on the response surface. Both types have their respective merits and problems. The error based selectivity is very general and very safe but its application to a range of samples (as opposed to a single sample) requires the knowledge of some constraint about the possible sample compositions. The selectivity concepts based on the response surface are easily applied to linear response surfaces but may lead to difficulties and counterintuitive results when applied to nonlinear response surfaces. A particular advantage of this class of selectivity is that with linear response surfaces it can provide a concentration independent measure of selectivity. In contrast, the error based selectivity concept allows only yes/no type decision about selectivity.

The relationship between the two classes of selectivity definitions has been derived for linear response surfaces (and with the necessary assumptions about the constraints of sample composition). It has been shown that the error based selectivity and the response surface based selectivity may be contradicting, i.e., a measurement classified as nonselective by using one definition may be perfectly selective according to the other definition.

If the response surface is nonlinear the selectivity concepts based on the response surface diverge and comparison with the error based selectivity becomes difficult. It has been shown here, however, that a practically relevant class of nonlinear response functions show in this respect the same behavior as the linear response functions. Therefore this type of nonlinear response function allows the use of a simply interpreted concentration-independent selectivity measure. Moreover it follows from our derivations that this is the only kind of nonlinear function making such simple interpretation possible.

Future research should investigate the response function of common analytical techniques and find the typical additional constraints used to limit the uncertainty of the result. From these one should derive, wherever possible, simple relationships between the parameters of the response function and the maximum error of the result. Notably such work has already been very successfully done in ion-selective potentiometry [18]. Interference by more than a single compound needs to be addressed, too.



The uncertainty arising from interference should also be related to the uncertainty due to limited precision in measuring the signal and the limited precision of the calibration. One should also clarify the relations to multivariate concepts of selectivity.

**Figure 1:** A general response surface ( $y$ : measured signal,  $c_i$ : analyte concentration,  $c_j$ : interferent concentration)

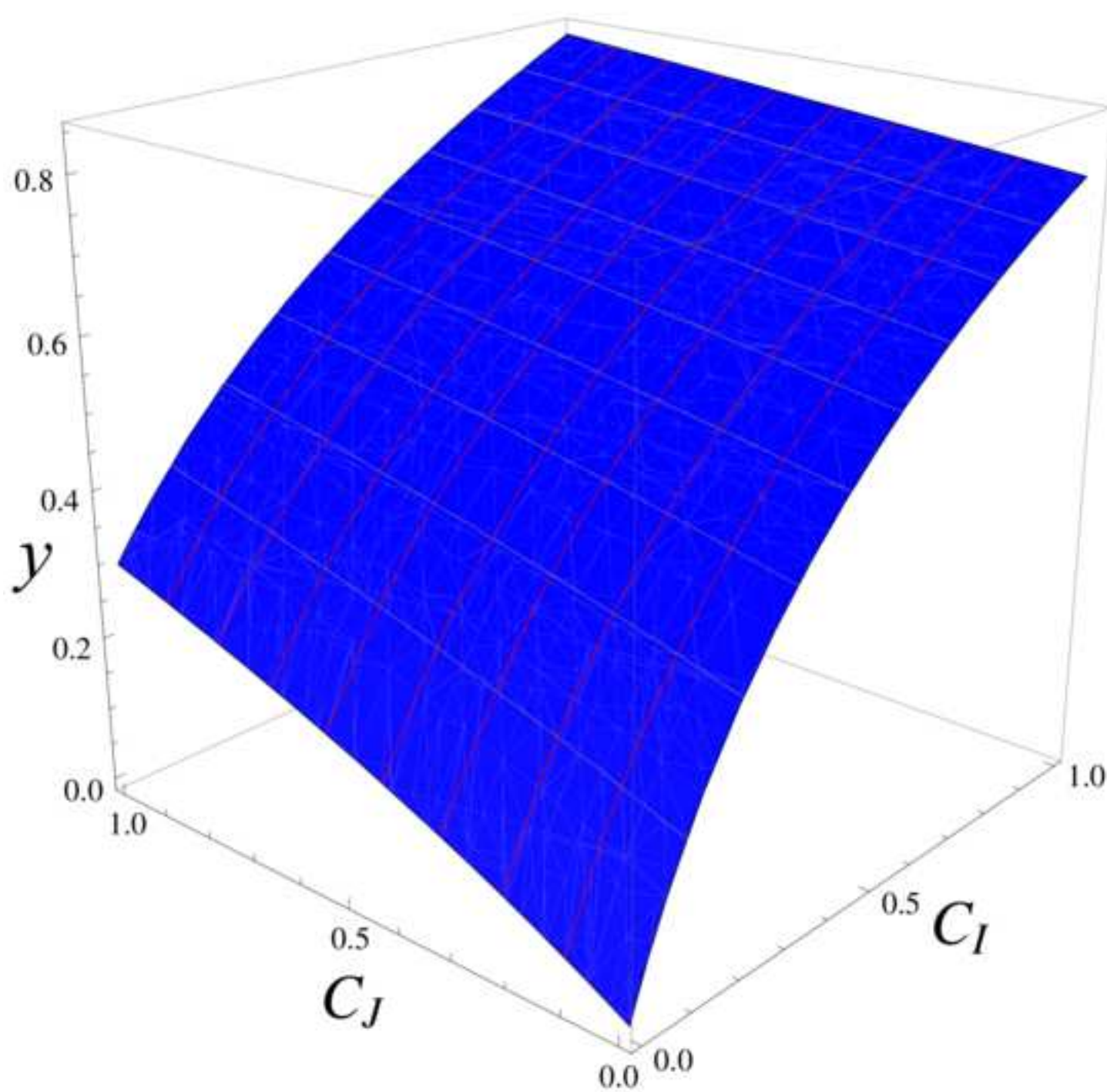
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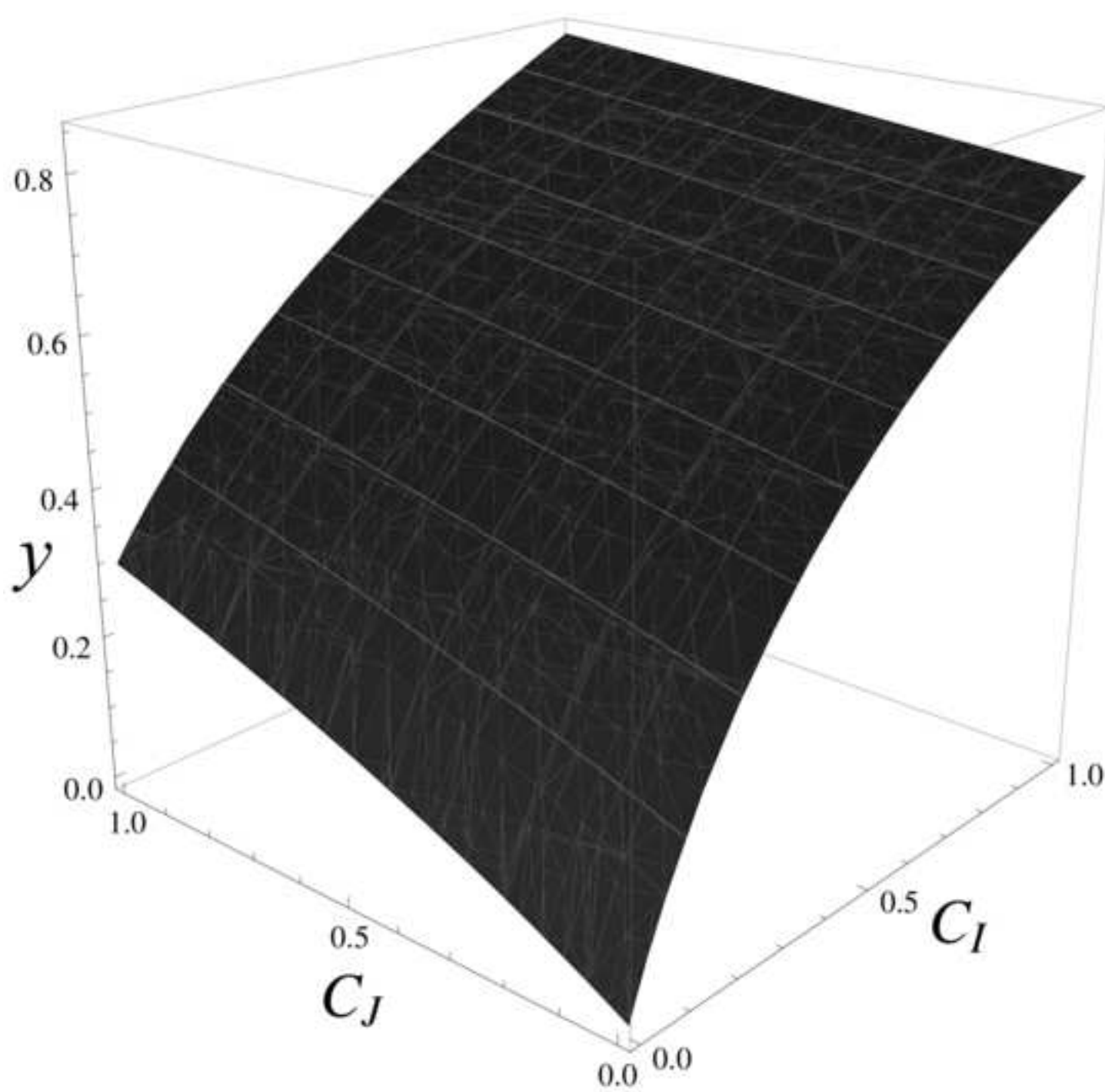
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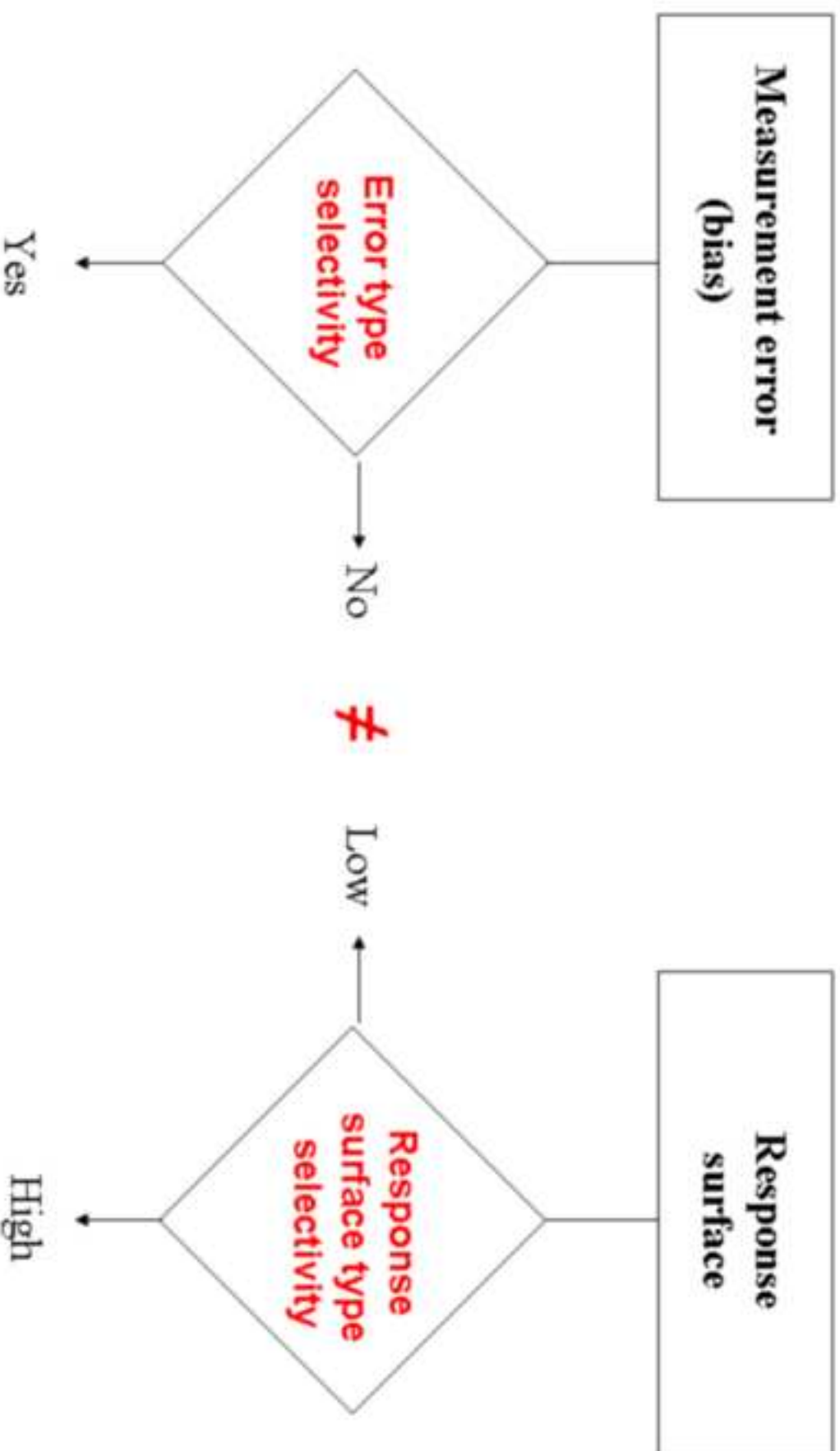
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**Figure 1:** A general response surface ( $y$ : measured signal,  $c_I$ : analyte concentration,  $c_J$ : interferent concentration)

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Highlights

for

**Selectivity in analytical chemistry: two interpretations for univariate methods**

by Dorko et al.

- Selectivity definitions are based on measurement error or on the response surface
- We give for the first time a comparative analysis of these two selectivity concepts
- Error based selectivity is a yes/no decision and assumes compositional constraints
- A selectivity measure can only be based on (pseudo)linear response surfaces
- Judgements on selectivity based on the two definitions may be contradicting